

FINAL REPORT  
TO THE  
U. S. ARMY RESEARCH OFFICE

September 2002

On the grant entitled

**"FIRST PRINCIPLES PREDICTIONS OF GUN TUBE EROSION CHEMISTRY AND  
POSSIBLE PROTECTIVE COATINGS"**

GRANT NO. DAAD9-99-1-0227

PROJECT PERIOD: 6/1/99 – 5/31/02

EMILY A. CARTER  
PRINCIPAL INVESTIGATOR

*Department of Chemistry and Biochemistry  
Box 951569  
University of California, Los Angeles  
Los Angeles, CA 90095-1569*

20030602 026

Approved for public release; distribution unlimited.

The views, opinions, and/or findings contained in this report are those of the author and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-1302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 09-01-2002	2. REPORT TYPE Final	3. DATES COVERED (From - To) 6/1/99-5/31/02
4. TITLE AND SUBTITLE  First Principles Predictions of Gun Tube Erosion Chemistry and Possible Protective Coatings		5a. CONTRACT NUMBER
		5b. GRANT NUMBER DAAD9-99-1-0227
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)  Emily A. Carter		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  University of California, Los Angeles Department of Chemistry and Biochemistry		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  US Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSOR/MONITOR'S ACRONYM(S) ARO
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)  <i>40051.10-CH</i>
12. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited		

## 13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

## 14. ABSTRACT

This final technical report summarizes results of this grant using first principles electronic structure methods to examine properties of:

- o Bulk cementite and its surfaces, a product of steel carburization that may play a role in gun tube erosion;
- o Carbon incorporation and diffusion in iron;
- o TiC, ZrC and BN interfaces with Fe, to investigate alternative protective coatings for gun tubes;
- o High temperature combustion dynamics;
- o Metal-insulator transitions in nanoparticle arrays.

In addition, we discuss progress made in developing new methods such as:

- o the ability to calculate local electronic excited states in or on metals
- o spin-dependent pseudopotentials that provide an accurate and less empirical description of Fe (and other magnetic transition metals)
- o local pseudopotentials and kinetic energy density functionals for linear scaling density functional theory
- o multiscale modeling methods coupling quantum mechanical models to mechanical engineering models of deformation and fracture

## 15. SUBJECT TERMS

density functional theory, pseudopotentials, iron, cementite, ceramic coatings, embedding theory, excited states, gun tube erosion, kinetic energy functionals

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 15	19a. NAME OF RESPONSIBLE PERSON Robert Shaw
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (include area code) (919) 549-4293

## Table of Contents

<b>Title Page</b>	<b>1</b>
<b>Table of Contents</b>	<b>2</b>
<b>Statement of Problem Studied</b>	<b>3</b>
<b>Summary of the Most Important Results</b>	<b>3</b>
<b>Publications</b>	<b>11</b>
<b>Participating Scientific Personnel</b>	<b>12</b>
<b>Inventions</b>	<b>12</b>
<b>Bibliography</b>	<b>13</b>

## Statement of the Problem Studied

Increasing the service lifetime of military machinery will improve logistics in the field (less down-time due to maintenance or replacement) and will free up resources for other pressing needs. To this end, the Army has a vested interest in enhancing the lifetime of gun barrels, which are limited currently by erosion of the steel from which the gun barrels are made. However, it is exceedingly difficult to determine experimentally *in situ* the mechanisms of erosion. Therefore, computer simulations can help elucidate those mechanisms and in ultimately extending the lifetime of gun barrels by discovering new ways to inhibit erosion.

As a result, in the past 3 years we undertook basic research to create new simulation tools and to investigate interfacial materials chemistry aspects of the gun tube erosion problem using first principles atomistic modeling techniques. In brief, we have developed minimal-adjustable-parameter first principles models of iron, accurate molecule-surface interaction theories, large-scale simulations of metals via linear scaling methods, and chemical-mechanical coupling via multiscale modeling to describe, e.g., hydrogen embrittlement in Fe. In terms of applications, we focused on the role of carburization: we examined bulk and surface properties of cementite,  $Fe_3C$ , thought to be a major culprit in gun tube erosion (GTE), as well as C incorporation and diffusion in Fe. We also studied ceramics as potential alternative coatings or possibly as liners to protect the gun tube.

## Summary of the Most Important Results

We now describe the most important findings during tenure of this grant from our applications of existing theoretical techniques to problems related to gun tube erosion, as well as to metal particles and high temperature combustion dynamics. Then we discuss new methods we developed that will allow more realistic simulations to be carried out in the future.

### *First Principles Simulations of Carburization*

Gun tube erosion involves the chemical degradation of steel, which is primarily iron (doped with 1% carbon). One possible mechanism for gun tube erosion is carburization, in which excess carbon is incorporated into steel (its source is likely from propellant byproducts, CO and  $CO_2$ ). Proposed mechanisms for the source of carbon include: reduction of CO by hydrogen to produce water and carbon atoms, methane dehydrogenation, and CO disproportionation. It is thought that the carbon diffuses into the steel and forms cementite,  $Fe_3C$ , which has a lower melting temperature than Fe by about 300 K. Thus one form of erosion is thought to be the formation of the lower melting point carbide, which then liquefies upon gun firing (temperatures around 1700 K), leading to erosion.

We studied bulk cementite and its low-index surfaces using first principles density functional theory (DFT).<sup>1</sup> This carbide is the most stable of all iron carbides, but it is

still metastable with respect to  $\alpha$ -Fe and graphite. Cementite has quite a complex crystal structure, with 16 atoms in the orthorhombic unit cell: four 6-coordinate carbon atoms, and two different types of 14-coordinate Fe atoms, eight of one type and four of the other. Spin-polarized DFT, using ultrasoft pseudopotentials and the generalized gradient approximation (GGA – critical here to obtain the correct bcc ground state of bulk Fe) for exchange and correlation, yields bulk lattice vectors within 0.03 Å of experiment; importantly, the lattice expands upon incorporation of C, which will introduce strain at the interface between cementite and steel. The bulk cohesive energy is within 6% of experiment. We predict some charge transfer from Fe to C in cementite, but it is still metallic (states near the Fermi level are Fe d-states, as in bulk iron). We also find a reduced magnetic moment compared to bulk Fe (this approximation to DFT reproduces the Fe magnetic moment to within  $0.25 \mu_B$  and the bulk modulus to within 10% of experiment).<sup>2</sup> The surface energies of Fe (ranging from  $2.3 - 2.6 \text{ J/m}^2$ ) follow the expected trends based on close-packing: for bcc, the (110) is the most stable, followed by (100), and then (111) is the least stable; for fcc, the most stable is the (111), followed by (110), and then (100) is the least stable. Seven low-Miller-index, stoichiometric (non-polar) surfaces of cementite were examined. The relative stability of these cementite surfaces correlates with surface smoothness: the more corrugated the surface, the higher the surface energy (the latter ranging between  $2.0-2.5 \text{ J/m}^2$ ). The surface energies of both Fe and cementite are very similar, because these cementite surfaces are dominated by Fe termination. All but two of the cementite surfaces have surface energies lower than the most stable bcc(110) surface of pure iron. This suggests that *lower surface energies may also provide a driving force for formation of cementite near the surface of steel, leading to a surface on a gun tube that can melt at lower temperatures than steel and erode away.*<sup>3</sup>

Recently, we began investigations into the mechanism of carbon incorporation into iron.<sup>4</sup> We began by studying C incorporation in austenite (fcc Fe), since the solubility of carbon is higher in austenite than in ferrite (bcc Fe) and therefore we can study C incorporation and diffusion in austenite with smaller simulation cells. We first verified that, within our DFT model (all-electron PAW DFT-GGA calculations), it is exothermic to dissolve C in Fe. We found that it is exothermic by  $0.1 - 0.2 \text{ eV/atom}$ , depending on the concentration (1-3% C). We then examined the diffusion of C from its preferred octahedral hollow site in austenite to a neighboring octahedral hollow. We find a barrier that is 0.2 eV too low compared to experiment ( $1.26 \text{ eV}$  compared to  $1.47 \text{ eV}$ ). At the moment that is at a  $\sim 3\%$  concentration level (1 C and 32 Fe atoms per unit cell); we are now examining the barrier at a lower concentration of  $\sim 1\%$  (1 C and 108 Fe atoms per unit cell) to see if the barrier is still too low. This provides a calibration of the DFT exchange-correlation energy, so that we can know approximately what errors we will expect in diffusion barriers when we begin to make predictions about impurity diffusion when the measured values are not available. Next we will study C diffusion in bcc Fe, and then move on to S diffusion predictions.

## ***First Principles Exploration of Alternative Protective Coatings for Steel***

In addition to examining failure mechanisms for gun tube erosion, we investigated possible alternative protective coatings for gun tubes. Chrome has been the liner of choice, but for environmental, as well as other, reasons, alternative protective coatings are desirable. We considered ceramic materials as candidates, since ceramics have been used in other extreme environment conditions quite successfully to protect metal components. Ceramics generally exhibit low thermal conductivity and have high melting points, two very positive traits for this application. In addition, we searched for ceramics that are very stable, do not undergo discontinuous phase transitions, have similar coefficients of thermal expansion to that of Fe, are narrow-range compounds (no variable composition), exhibit good mechanical properties, are environmentally friendly, and potentially adhere strongly to iron. After scanning known properties of various ceramics, we selected three ceramics on which to focus: TiC, ZrC, (both crystallize in the NaCl structure) and cubic BN, as they all exhibit excellent mechanical properties (hardness, etc.), have very high melting points ( $>3000^{\circ}\text{C}$ ), thermal conductivities at least one order of magnitude lower than that of the current chrome coating, and quite similar coefficients of thermal expansion to that of steel ( $\sim 10^{-5}/^{\circ}\text{C}$ ). DFT-GGA theory yields bulk properties of these ceramics (lattice parameters, bulk moduli, and energies of formation) within 10% of experiment.<sup>5,6,7,8</sup> Among these crystals, we find that only c-BN exhibits a band gap, while the others are metals. Analysis of the densities of states indicates that TiC and ZrC exhibit a mixture of ionic, covalent, and metallic character, while c-BN is polar covalent in nature. We observe the effects of charge transfer in our studies of the surfaces of these ceramics, where we find that the stoichiometric, nonpolar (100) surfaces of TiC and ZrC and c-BN(110) are by far the most stable.<sup>5,6,7,8</sup> We then examined the adhesion of c-BN(110), TiC(100), and ZrC(100) coatings to the most stable face of  $\alpha$ -Fe, bcc Fe(110). The bcc Cr-bcc Fe interface was also investigated for comparison. The interfaces for the metal carbide coatings with Fe are dominated by strong Fe-C interactions, while the BN coating exhibits stronger Fe-N than Fe-B interactions. We predict that TiC is the most strongly adhered of the three coatings, with an ideal work of adhesion of  $2.6\text{ J/m}^2$ . ZrC and BN coatings have much weaker adhesion,  $\sim 1.5\text{ J/m}^2$ . This suggests *TiC is the best candidate for an alternative to Cr*. However, even the TiC work of adhesion is lower by nearly a factor of 2 compared to the minimum energy required to crack Fe (using the Griffith criterion, which ignores plastic deformation – hence the “minimum” denotation), which suggests that the coating may not be as strongly adhered as might be needed. Our calculations do indicate one reason why Cr is a good coating: the interfacial adhesion energy of Cr to Fe ( $5.0\text{ J/m}^2$ ) is larger than the minimum energy required ( $4.5\text{ J/m}^2$ ) to crack Fe (though smaller than the minimum energy required to crack Cr,  $5.4\text{ J/m}^2$ ). *Though the iron-ceramic bonding is weaker than the Cr-Fe adhesion, the superior protective properties of these ceramics might warrant them to be considered as an alternative to Cr.*

## ***First Principles Studies of the Metal-Insulator Transition in Metal Nanoparticle Arrays***

Optical reflectivity experiments<sup>9</sup> showed that metal nanoparticles in an ordered two-dimensional array undergo a transition from an insulating phase to a conducting phase upon compression of the array (via a Langmuir trough). It was thought that the overlap of the nanoparticle wavefunctions when the array was compressed (leading to smaller particle-particle separations) led to the observed electronic transition. Prior to our work, first principles calculations had not been performed to try to determine the mechanism of the transition because the number of atoms required to simulate such a system runs into the many hundreds to thousands of atoms. We have a DFT technique that can treat main group metals within a linear scaling formalism, as described in more detail later. This means that if we double the number of electrons treated, we only double the cost of the calculation. Conventional DFT scales cubically with the number of electrons and hence only small (<100 atom) particles can be treated.

We carried out a series of calculations on a hexagonally periodic array of  $\text{Al}_{249}$  clusters, with two such clusters in the unit cell. This provides nanoparticles 20 Å in diameter, similar to the size of the particles created experimentally. What we were able to do, within this Hohenberg-Kohn type DFT, is to self-consistently solve directly for the density of the ~1500 valence electrons in this nanoparticle unit cell, at varying interparticle separations.<sup>10</sup> We then used this density to estimate the wavefunction overlap between each nanoparticle, and this was in turn used in a tight-binding model to ascertain at what interparticle separation the band gap closed. We find a large band gap at large separation - consistent with the observed insulating behavior. Then, as the separation decreases to about 20% greater than the particle's diameter, the band gap goes to zero and the insulator-to-metal transition occurs. This is entirely consistent with measurements on Ag particles of similar size (26 Å diameter). So we have captured the correct physics with our DFT method. Moreover, we noticed that the overlap of the wavefunctions at the point at which the gap closes is extremely small, which means that *very tiny overlaps of the electronic wavefunctions between nanoparticles are sufficient to allow conductivity of electrons across a nanoparticle array.*

## ***Ab Initio Molecular Dynamics of Vinylidene-Acetylene Isomerization***

As a first step toward studying the dynamics of hot gases, we examined a process important in acetylene torches: the isomerization of vinylidene to acetylene and vice-versa. It turns out that if one ignores this process in analyzing the kinetics of acetylene combustion, one derives completely the wrong thermochemistry for acetylene. Thus this reaction is an important one for the complete picture of acetylene combustion. We performed complete active space self-consistent field (CASSCF) ab initio molecular dynamics (AIMD) simulations of the preparation of vinylidene, and its subsequent, highly exothermic isomerization to acetylene, via electron removal from

vinylidene anion ( $D_2C=C^- \rightarrow D_2C=C: \rightarrow DC\equiv CD$ ).<sup>11</sup> Remarkably, we find that only 20% of the vinylidenes generated this way isomerized, suggesting average lifetimes  $> 1$  ps for vibrationally excited vinylidene- $d_2$ . Since the anion and neutral vinylidene are structurally similar, and yet extremely different structurally from the isomerization transition state (TS), neutral vinylidene is *not* formed near the TS so that it must live until it is in a state prepared to cross the barrier. The origin of the delay is explained via both orbital rearrangement and intramolecular vibrational energy redistribution (IVR) effects. Unique signatures of the isomerization dynamics are revealed in the anharmonic vibrational frequencies extracted from the AIMD, which should be observable by ultrafast vibrational spectroscopy and in fact are consistent with currently available experimental spectra. Most interestingly, of those trajectories that did isomerize, *every one of them violated conventional transition state theory by recrossing back to vinylidene multiple times, against conventional notions that expect highly exothermic reactions to be irreversible*. The dynamical motion responsible for the multiple barrier recrossings involves *strong mode-coupling* between the vinylidene  $CD_2$  rock and a local DCC bend mode that has been recently observed experimentally. Lastly, the multiple barrier recrossings can be used, via a *generalized definition of lifetime*, to reconcile extremely disparate experimental estimates of vinylidene's lifetime (differing by at least six orders of magnitude). Thus, we once again demonstrated the usefulness of ab initio molecular dynamics to reveal behavior far beyond what a simple study of the potential energy surface would predict. Such studies will be carried out for the hot propellant gases involved in gun tube erosion in the future.

### **Development of Electronic Structure Theories for the Condensed Phase**

This section describes the continued development of good solid-state models for metals and molecules interacting with metals. This work consists of improvements to both the *scaling* of density functional theory (DFT)<sup>12</sup> via the development of accurate kinetic energy functionals,<sup>13,14,15</sup> the *accuracy* of ground state DFT via systematic corrections to it in a local region (e.g., where a chemical bond is breaking or forming), as well as the ability to calculate local excited states on or in metals.<sup>16,17,18</sup> It also consists of improved descriptions of the effect of the core electrons on the valence electrons via *spin-dependent pseudopotentials*.<sup>19,20</sup> We are also working linking our atomistic simulations to larger length scale mechanical engineering simulations of cracking.<sup>21,22,23</sup> On-the-fly linking of our linear scaling DFT theory for metals to the quasicontinuum method for treating deformations of solids has been achieved.<sup>24</sup> This will allow more realistic simulations of large-scale gun tube erosion to be tackled in the future.

#### ***Kinetic Energy Density Functionals (KEDF's)***

It is possible to approximately solve the Schrödinger equation directly for the electron density. In order to do this, one must have not only an expression for the exchange-correlation energy, but also one for the kinetic energy, in terms of the density.

Recently, we developed new KEDF's that satisfy both smoothly varying and rapidly varying density limits of exact linear response theory.<sup>13,14</sup> These new functionals yield accurate structures, energy differences, vacancy formation energies, densities, and even surface energies and densities (where accuracy is relative to Kohn-Sham DFT, since the KEDF's are an approximation to K-S DFT). The advantage of the density-only DFT method is that the cost of the method scales linearly with the size of the system, allowing one to solve for the electron densities and properties of thousands of atoms; moreover, it is the only such method available for treatment of metallic systems. As mentioned above, we used these new functionals to examine the electronic structure of nanoparticle arrays, work that would have been impossible with K-S DFT and would not have been accurate with previous KEDF's.<sup>10</sup> Further work is in progress to extend these KEDF's to nonmetallic systems, but this is an extremely difficult problem.

We recently wrote a review of all the issues associated with KE DFT,<sup>15</sup> where we make it clear that the two outstanding issues are: (i) how to constrain these KE functionals further to treat localized electron densities and (ii) accurate pseudopotentials (which represent the screened ion-valence electron interaction) need to be developed that are local in nature (i.e., only depend on one coordinate and do not involve projection operators that must act on a wavefunction). Regarding the first point, we are examining the use of the idempotency constraint on the density to see if this will help constrain the KE functionals, to make them applicable to nonmetallic systems. Our efforts in the last two years have focused more intensely on the second point, because the way to proceed was clearer. We developed local pseudopotentials derived by inverting the Kohn-Sham equations and finding a pseudopotential that reproduces a Kohn-Sham (orbital-based DFT) density for both atoms<sup>25</sup> and bulk environments.<sup>26</sup> In particular, we have shown that accurate, transferable local pseudopotentials for an element that is not at all nearly-free-electron-like can be developed by inversion of the Kohn-Sham equations and exploiting the first Hohenberg-Kohn theorem. The latter states that given a density there is a one-to-one mapping of the exact potential associated with that density. Thus, given a high quality density (we use Kohn-Sham DFT densities from nonlocal norm-conserving pseudopotential calculations), one should be able to find the exact Kohn-Sham effective potential that reproduces that density. Unfortunately, this is an inverse problem with no unique solution. We tried many algorithms that have been suggested, and found the one due to Wang and Parr to be the most stable. We first utilized this approach, which updates a guessed potential utilizing the target density, the current iteration's orbitals and eigenvalues, in the context of atoms only. We then worked out a scheme to do the same thing given a target bulk density (this is nontrivial as the only data points available are at the Bragg vectors for a given crystal structure). We now have a robust algorithm in the solid state for this purpose and have shown that we can produce accurate, transferable local pseudopotentials that reproduce nicely, within Kohn-Sham DFT, the phase orderings of 8 different phases of Si predicted by nonlocal pseudopotentials within Kohn-Sham DFT. When we now use this local pseudopotential in orbital-free DFT calculations of different phases of Si, any errors incurred have now been isolated to only the kinetic energy density

functional. This provides the means to then move forward in improving KE density functionals for nonmetals.

As a last note, in the summer of 2002, there was workshop at CECAM in Lyon, France, devoted to kinetic energy density functionals. The P.I. was invited to speak, but instead sent her former postdoc, Alex Wang, and a current graduate student, Baojing Zhou to the meeting. Alex Wang talked about these new kinetic energy density functionals and their applications, and Baojing Zhou presented a poster on deriving ab initio local pseudopotentials based on Kohn-Sham nonlocal pseudopotential bulk densities. The P.I. later heard from more than one senior participant that the P.I.'s KEDF's remain the state-of-the-art and the most advanced/accurate available today.

### *Spin-Dependent Pseudopotentials*

In order to correctly model Fe, Cr, and compounds of Fe, it is critical to capture the ferromagnetic nature of Fe and (at least) the local anti-ferromagnetic behavior of Cr correctly within DFT, since DFT is our starting point for all other calculations. Efficient solid-state DFT calculations employ plane-wave basis sets, which describe the valence electrons, and pseudopotentials, which represent the nucleus and associated core electrons. Generally, a nonmagnetic reference state is used to construct such pseudopotentials. Unfortunately, when such pseudopotentials are used for transition metals, large errors occur in the description of the d-electrons (though the nonlinear core correction to exchange-correlation reduces these errors, at the expense of introducing more parameters). We have ameliorated this problem by developing spin-dependent, norm-conserving pseudopotentials.<sup>27</sup> These pseudopotentials, containing both a nonmagnetic term and a part that depends self-consistently on the spatially varying net spin polarization (with no additional parameters), greatly improve the transferability of the pseudopotential compared to traditional formulations. Not only do they accurately reproduce atomic state splittings for the entire first and second row transition series, but we have shown they reproduce reasonably well the structural properties of bulk Fe, Co, and Ni.<sup>19</sup> Moreover, the predicted magnetic moment is much closer to experiment when the spin-dependent pseudopotentials are employed. We have now implemented these pseudopotentials in a reciprocal-space bulk DFT code (CASTEP),<sup>28</sup> which is considerably more efficient than the real space bulk code in which we first implemented the method. The advantage of these pseudopotentials is that they provide the same degree of accuracy without introducing a plethora of empirical parameters needed by other approaches. The disadvantage is they have a somewhat higher cost associated with their use. To the extent that one prefers to minimize the number of empirical parameters in a method, this approach is aesthetically more pleasing. In addition, the embedding theory below requires the use of so-called norm-conserving pseudopotentials, which necessitates the use of these (norm-conserving) spin-dependent pseudopotentials for Fe-containing materials.

## ***Embedding Theory for Accurate Energetics in a Local Region of Condensed Matter***

While one can go far studying metals using the state-of-the-art in condensed matter electronic structure, namely periodic DFT, there are times when DFT fails inexplicably, due to the approximations made in accounting for electron exchange and correlation. We developed a method that improves upon the DFT result by means of explicit convergence of electron correlation (via perturbation theory and CI). The Army Research Office (ARO) helped support the development of this theory where a metal cluster is embedded into a periodic slab representation of the infinite metallic conductor. We demonstrated that this systematically improves the description of electron correlation in a local region, over that offered by DFT.<sup>29</sup> In practice, a local region of the solid is represented by a small cluster, for which high quality quantum chemical calculations are performed. The interaction of the cluster with the extended condensed phase is taken into account by an effective embedding potential. This potential is constructed within periodic DFT and is used as a one-electron operator in subsequent cluster calculations. This was done originally within the context of HF and Møller-Plesset perturbation theories (MP-n) through fourth order for improved descriptions of electron exchange and correlation in electronic ground states, but recently we extended it to provide also a fairly accurate description of localized excited states in condensed matter.<sup>16,17,18</sup> Such local excited states have not been accessible from *ab initio* theory for metallic systems before this work. Among a variety of benchmark calculations, we investigated a CO molecule adsorbed on a Pd(111) surface. By performing CASSCF, CI, and MP-n theories, we not only were able to obtain accurate adsorption energies via local corrections to DFT, but also vertical excitation energies, e.g., for an internal ( $5\sigma \rightarrow 2\pi^*$ ) excitation within the adsorbed CO molecule. We have shown that the agreement with experimental electron energy loss spectra (EELS) improves dramatically upon use of the CI embedding theory, compared to CI calculations on finite clusters. Thus, we demonstrated that our new scheme provides fairly accurate predictions of local excited states on metal surfaces, as well as a systematic means of improving locally on ground state properties.

Work in progress on the embedding theory involves: (i) calculation of forces such that CASSCF dynamics of molecules impinging and reacting on metal surfaces will be possible (the coding for this is nearly done and partially tested); (ii) exploration of the robustness of the kinetic energy functional potentials used in the embedding potential, when applied to other materials (currently we are examining this for Al, Cu, and Pt surfaces); and (iii) extension of the embedding theory to MRSDCI (currently we have developed the ability to get CI natural orbitals and are implementing the calculation of CI densities from the natural orbitals, so that we can construct the cluster only terms of the embedding potential from a MRSDCI density).

This theory will be used to refine diffusion and reaction energetics on Fe surfaces and to examine propellant by-product surface and bulk chemistry on Fe in the years to come.

### ***Bridging Length Scales in Materials Simulations***

We are funded elsewhere to work on the bridging length scales problem, however the work in that arena will have considerable impact on our ability to model gun tube erosion, and so our progress in this area is briefly described here. First, we are collaborating with Michael Ortiz, a Professor in the Graduate School of Aeronautics at Caltech, to link our atomistic information to micron-to-mm scale materials failure. This is being tackled in two ways. The first is by what may be referred to as an informed continuum model, in which information from the atomic scale is used as input into a separate continuum level simulation of crack propagation. We have calculated the force laws that describe how cracks form in metals and oxidized or embrittled metals and have formulated, via renormalization group theory, a means of rescaling the atomic scale forces involved in crack opening up to an effective force law for the microscale. This work promises to introduce chemical effects on mechanical materials failure for the first time.<sup>23</sup> Work in progress includes calculating the critical opening displacement, maximum tensile stress, and work of adhesion as a function of hydrogen concentration in steel. We are developing a coupled diffusion/cracking model for hydrogen embrittlement in steel.<sup>30</sup>

Secondly, we developed an on-the-fly coupling of electrons/atoms to a micron scale mechanical engineering model, via linking our linear scaling orbital-free DFT code to a local quasicontinuum code (which seamlessly goes from a finite element averaged description of millions of atoms down to nanometer resolution where needed). What is required is the ability to treat bulk unit cells of arbitrary distortions and to compute the stress tensor on that cell, neither of which was implemented in our OF-DFT code. The idea is that the deformations of each DFT cell are determined by the quasicontinuum method while the DFT calculations provide the stress tensors to the quasicontinuum code to determine how to next deform each finite element node. We have carried out nanoindentation simulations of Al thus far.<sup>24</sup> We should be able to predict hardness of metal alloys, in the presence of, e.g. precipitates, in this way.

Thirdly, we are developing an informed continuum approach to martensitic phase transformations in steel, by calculating the elastic properties, interfacial energies, and transition paths for pressure-induced bcc to hcp transitions in Fe.<sup>31</sup>

These new software tools will allow us to model, e.g., shock wave deformations in Fe and chemically-induced cracking of Fe.

## Publications Under ARO Sponsorship

1. S. C. Watson and E. A. Carter, "Linear Scaling Parallel Algorithms for the First Principles Treatment of Metals," *Computer Physics Communications*, **128**, 67 (2000).
2. Y. A. Wang and E. A. Carter, "Orbital-Free Kinetic Energy Density Functional Theory," in "Theoretical Methods in Condensed Phase Chemistry," S. D. Schwartz, Ed., within the series "Progress in Theoretical Chemistry and Physics," Kluwer, 117-84 (2000).
3. R. L. Hayes, E. Fattal, N. Govind, and E. A. Carter, "Long Live Vinylidene! A New View of the  $H_2C=C \rightarrow HCCH$  Rearrangement from Ab Initio Molecular Dynamics," *J. Am. Chem. Soc.*, **123**, 641 (2001).
4. T. Klüner, N. Govind, Y. A. Wang, and E. A. Carter, "Prediction of Electronic Excited States of Adsorbates on Metal Surfaces from First Principles," *Phys. Rev. Lett.*, **86**, 5954 (2001).
5. F. Starrost and E. A. Carter, "Quantum Structural Methods for the Solid State and Surfaces," in the *Encyclopedia of Chemical Physics and Physical Chemistry*, J. H. Moore and N. Spencer, Eds. (Institute of Physics), **2**, 1947 (2001).
6. F. Starrost, H. Kim, S. C. Watson, E. Kaxiras, and E. A. Carter, "Density Functional Theory Modeling of Bulk Magnetism with Spin-Dependent Pseudopotentials," *Phys. Rev. B*, **64**, 235105 (2001).
7. T. Klüner, N. Govind, Y. A. Wang, and E. A. Carter, "Periodic Density Functional Embedding Theory for Complete Active Space Self-Consistent Field and Configuration Interaction Calculations: Ground and Excited States," *J. Chem. Phys.*, **116**, 42 (2002).
8. T. Klüner, N. Govind, Y. A. Wang, and E. A. Carter, "Reply to the Comment on 'Prediction of Electronic Excited States of Adsorbates on Metal Surfaces from First Principles', *Phys. Rev. Lett.*, **86**, 5954 (2001) by Klüner et al." *Phys. Rev. Lett.*, **88**, 209702 (2002).
9. W. Chiou, Jr. and E. A. Carter, "Structure and Stability of  $Fe_3C$ -Cementite Surfaces from First Principles," *Surf. Sci.*, submitted (2002).
10. A. Arya and E. A. Carter, "Structure, Bonding, and Adhesion at the  $TiC(100)/Fe(110)$  Interface from First Principles," *Phys. Rev. B*, submitted (2002).

## Participating Scientific Personnel (\* indicates those supported financially)

Prof. Emily A. Carter,\* Principal Investigator  
Dr. Niranjan Govind,\* Postdoctoral Fellow  
Dr. Stuart Watson, Postdoctoral Fellow  
Dr. Eyal Fattal, Postdoctoral Fellow  
Dr. Alex Wang, Postdoctoral Fellow  
Dr. Frank Starost, Postdoctoral Fellow  
Dr. Thorsten Kluener, Postdoctoral Fellow  
Dr. Ashok Arya,\* Postdoctoral Fellow  
Dr. Kyle Caspersen, Postdoctoral Fellow  
Mr. Wun Chiou, Jr.,\* graduate student  
Mr. Vincent Coclua,\* graduate student  
Mr. De-en Jiang,\* graduate student

## Inventions

Development of the following algorithms and codes:

- Local pseudopotentials for use in our orbital-free density functional method, derived by inverting the Kohn-Sham equation
- Generalization of our orbital-free density functional code to treat non-orthorhombic cells and to compute the stress tensor, in order that arbitrarily deformed simulation cells may be treated
- spin-dependent pseudopotentials in the Kleinman-Bylander form for use in both real and reciprocal space solid state density functional theory codes.
- An embedding theory of ground and excited states in bulk metals and metal surfaces
- Coupled orbital-free density functional/finite element code for multiscale modeling of deformations of micron size samples of metal

## Bibliography

<sup>1</sup> F. Starost and E. A. Carter, "Quantum Structural Methods for the Solid State and Surfaces," in the *Encyclopedia of Chemical Physics and Physical Chemistry*, J. H. Moore and N. Spencer, Eds. (Institute of Physics), **2**, 1947 (2001).

<sup>2</sup> One other DFT paper on bulk cementite has appeared: J. Häglund, G. Grimvall, and T. Jarlborg, "Electronic structure, x-ray photoemission spectra, and transport properties of  $Fe_3C$  (cementite)," *Phys. Rev. B* **44**, 2914 (1991). In addition, an empirical tight-binding study of bulk iron carbides, including cementite, is available: A. H. Cottrell, "A theory of cementite," *Mat. Sci. Tech.* **9**, 277 (1993). We are in good agreement with this earlier work (LMTO-LDA) for its magnetic properties and structure.

<sup>3</sup> W. Chiou, Jr. and E. A. Carter, "Structure and Stability of  $Fe_3C$ -Cementite Surfaces from First Principles," *Surface Sci.*, submitted (2002).

<sup>4</sup> D. Jiang and E. A. Carter, work in progress (2002).

<sup>5</sup> A. Arya and E. A. Carter, "Structure, Bonding, and Adhesion at the  $TiC(100)/Fe(110)$  Interface from First Principles," *Phys. Rev. B*, submitted (2002)

<sup>6</sup> A. Arya and E. A. Carter, *Surf. Sci.*, to be submitted (2002).

<sup>7</sup> A. Arya and E. A. Carter, *J. Chem. Phys.*, to be submitted (2002).

<sup>8</sup> A. Arya and E. A. Carter, *Mod. Sim. Mat. Sci. and Eng.*, to be submitted (2002).

<sup>9</sup> C. P. Collier et al., *Science*, **277**, 1978 (1997).

<sup>10</sup> S. C. Watson and E. A. Carter, "Linear-Scaling Parallel Algorithms for the First Principles Treatment of Metals," *Comp. Phys. Comm.*, **128**, 67 (2000).

<sup>11</sup> R. L. Hayes, E. Fattal, N. Govind, and E. A. Carter, "Long Live Vinylidene: A New View of the  $H_2C=C \rightarrow HC=CH$  Rearrangement from Ab Initio Molecular Dynamics," *J. Am. Chem. Soc.*, **123**, 641 (2001).

<sup>12</sup> S. C. Watson and E. A. Carter, "Linear Scaling Parallel Algorithms for the First Principles Treatment of Metals," *Computer Physics Communications*, **128**, 67 (2000).

<sup>13</sup> Y. A. Wang, N. Govind, and E. A. Carter, "Orbital-Free Kinetic Energy Functionals for the Nearly-Free Electron Gas," *Phys. Rev. B*, **58**, 13465 (1998).

<sup>14</sup> Y. A. Wang, N. Govind, and E. A. Carter, "Orbital-Free Kinetic-Energy Density Functionals with a Density-Dependent Kernel," *Phys. Rev. B*, **60**, 16350 (1999).

<sup>15</sup> Y. A. Wang and E. A. Carter, "Orbital-Free Kinetic Energy Density Functional Theory," in "Theoretical Methods in Condensed Phase Chemistry," S. D. Schwartz, Ed., within the series "Progress in Theoretical Chemistry and Physics," Kluwer, 117-84 (2000).

<sup>16</sup> T. Klüner, N. Govind, Y. A. Wang, and E. A. Carter, "Prediction of Electronic Excited States of Adsorbates on Metal Surfaces from First Principles," *Phys. Rev. Lett.*, **86**, 5954 (2001).

<sup>17</sup> T. Klüner, N. Govind, Y. A. Wang, and E. A. Carter, "Periodic Density Functional Embedding Theory for Complete Active Space Self-Consistent Field and Configuration Interaction Calculations: Ground and Excited States," *J. Chem. Phys.*, **116**, 42 (2002).

<sup>18</sup> T. Klüner, N. Govind, Y. A. Wang, and E. A. Carter, "Reply to the Comment on 'Prediction of Electronic Excited States of Adsorbates on Metal Surfaces from First Principles', *Phys. Rev. Lett.*, **86**, 5954 (2001) by Klüner et al." *Phys. Rev. Lett.*, **88**, 209702 (2002).

---

<sup>19</sup> F. Starrost, H. Kim, S. C. Watson, E. Kaxiras, and E. A. Carter, "Density Functional Theory Modeling of Bulk Magnetism with Spin-Dependent Pseudopotentials," *Phys. Rev. B*, **64**, 235105 (2001).

<sup>20</sup> V. Coclà, F. Starrost, S. C. Watson, and E. A. Carter, "Spin-Dependent Pseudopotentials in the Solid State Environment," manuscript in preparation.

<sup>21</sup> E. A. A. Jarvis, R. L. Hayes, and E. A. Carter, "Effects of Oxidation on the Nanoscale Mechanisms of Crack Formation in Aluminum," *ChemPhysChem*, **2**, 55 (2001).

<sup>22</sup> F. Starrost and E. A. Carter, "Modeling the Full Monty: Baring the Nature of Surfaces Across Time and Space," *Surface Sci.* **500**, 323 (2002).

<sup>23</sup> S. Serebrinsky, O. Nguyen, M. Ortiz, R. L. Hayes, E. A. A. Jarvis, and E. A. Carter, work in progress.

<sup>24</sup> R. L. Hayes, M. Fago, F. Starrost, M. Ortiz, and E. A. Carter, to be published.

<sup>25</sup> Y. A. Wang and E. A. Carter, "Ab Initio Local Pseudopotentials for Orbital-Free Density Functional Theory Calculations," manuscript in preparation (2002).

<sup>26</sup> B. Zhou, Y. A. Wang, and E. A. Carter, "First Principles Local Pseudopotentials Derived from a Bulk Environment," manuscript in preparation (2002).

<sup>27</sup> S. C. Watson and E. A. Carter, "Spin-Dependent Pseudopotentials," *Phys. Rev. B*, **58**, R13309 (1998).

<sup>28</sup> V. Coclà, F. Starrost, S. C. Watson, and E. A. Carter, manuscript in preparation.

<sup>29</sup> N. Govind, Y. A. Wang, A. J. R. da Silva, and E. A. Carter, "Accurate Ab Initio Energetics of Extended Systems via Explicit Correlation Embedded in a Density Functional Environment," *Chem. Phys. Lett.*, **295**, 129 (1998); N. Govind, Y. A. Wang, and E. A. Carter, "Electronic Structure Calculations by First Principles Density-Based Embedding of Explicitly Correlated Systems," *J. Chem. Phys.* **110**, 7677 (1999).

<sup>30</sup> S. Serebrinsky, K. Caspersen, E. A. Carter, and M. Ortiz, work in progress.

<sup>31</sup> K. Caspersen, A. Lew, M. Ortiz, and E. A. Carter, work in progress.